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Determining how atmospheric carbon dioxide concentrations have changed during the history of the Earth

Marcus P. S. Badger, Richard D. Pancost and Timothy G. Harrison

ABSTRACT The reconstruction of ancient atmospheric carbon dioxide concentrations is essential to understanding the history of the Earth and life. It is also an important guide to identifying the sensitivity of the Earth system to this greenhouse gas and, therefore, constraining its future impact on climate. However, determining the concentration of CO₂ in ancient atmospheres is a challenging endeavour requiring the application of state-of-the-art analytical chemistry to geological materials, underpinned by an understanding of photosynthesis and biochemistry. It is truly an interdisciplinary challenge.

Carbon dioxide and water vapour are the two largest contributors to the greenhouse effect in the atmosphere. Water vapour is so close to its condensation point in the atmosphere that it is difficult to increase its concentration without raising the temperature. In contrast, the concentration of CO₂ in the atmosphere ($p\text{CO}_2$) can be changed by altering the balance between its sources and sinks. Thus, although CO₂ is only a minor component in the atmosphere compared with water vapour (390 parts per million (ppm) compared with up to 40 000 ppm), changes in its concentration due to natural and human activity are possible and important controls on greenhouse warming.

Carbon exists on Earth in various reservoirs, most importantly the biosphere, sedimentary rocks and the ocean–atmosphere system. Movements of carbon between these reservoirs are governed by a number of processes. Firstly, growth of the biosphere and the marine ‘biological pump’ can transfer carbon from the ocean–atmosphere system to sediments, and can remove CO₂ from the atmosphere. Secondly, vulcanism has multiple impacts but primarily transfers carbon from the buried sedimentary reservoir back into the ocean–atmosphere system. Thirdly, the chemical weathering of rocks can either remove carbon from the atmosphere system or add it, depending on the nature of the rocks being weathered.

Finally, within the ocean–atmosphere system itself, CO₂ can be moved either into or out of the atmosphere depending on the balance of ocean carbonate chemistry and circulation. Crucially, the balance of these sources and sinks changes over time, and any imbalance can cause either a ‘draw-down’ or an increase in $p\text{CO}_2$.

Movements of significant amounts of carbon between reservoirs happen on long, geological timescales, and natural variations in the global carbon cycle have caused CO₂ concentrations to rise and fall in the atmosphere over the last 2 billion years. More recently, $p\text{CO}_2$ has started to increase owing to the burning of fossil fuels by humans. This anthropogenic input has caused $p\text{CO}_2$ to rise from a pre-industrial age value of 270–280 ppm to 391 ppm in 2011. Although it is highly likely that this rise in $p\text{CO}_2$ has caused the small increase in observed temperature over the last century, there is legitimate debate about the effect of increasing $p\text{CO}_2$ over the next century and beyond. One approach to examine what the Earth’s climate system would be like at higher $p\text{CO}_2$ levels is to look at what the climate was like during periods of Earth’s history when it was higher than today. To do so requires an understanding of how atmospheric CO₂ has evolved over the past few million years. For the past 800 000 years, $p\text{CO}_2$ can be measured by analysing remnants of ancient atmosphere trapped

in tiny gas bubbles found in polar ice (Petit *et al.*, 1999; Siegenthaler *et al.*, 2005; Luthi *et al.*, 2008). Ice core records have revealed that $p\text{CO}_2$ varied during glacial and interglacial cycles – with higher concentrations during the latter. Most of this change appears to be a positive feedback – an amplification of small changes in temperature, paced by periodic variations in the Earth's orbit around the Sun.

Ice core records can go no further back than about 850 000 years, the age of the oldest ice at the base of the major ice sheets on Greenland and Antarctica. Therefore, to look into deeper time we must rely on proxy records. Geochemical proxies are chemical signatures preserved in the geological record from which we can derive

information about past environmental conditions. Here we describe an approach to reconstruct past atmospheric CO₂ concentrations using the isotopic composition (see Box 1) of algal lipids. It requires an appreciation of the biology of algae, the chemistry of photosynthesis, the geology represented by the rocks in which the compounds are found, and the analytical chemistry required to make these challenging measurements.

A method for extending the record beyond 800 000 years: isotope discrimination during photosynthesis

All plants, including algae, convert CO₂ to simple sugars during photosynthesis. Photosynthesis is the basis for life on Earth and is responsible for

BOX 1 Carbon isotopes

Many elements in nature have isotopes; these are atoms with the same number of protons but a different number of neutrons. As each isotope has the same number of protons, they are chemically identical to each other but the different masses of the isotopes mean that they react at slightly different rates (causing what is known as a kinetic isotope effect, KIE). Carbon has three natural isotopes, of which two are stable: ¹²C, which has six protons and six neutrons, and ¹³C, which has one extra neutron and makes up about 1% of all carbon. Carbon also has one naturally occurring radioactive isotope, ¹⁴C, which has eight neutrons and is produced when cosmic rays interact with nitrogen molecules in the upper atmosphere. This radioactive carbon has a half-life of 5730 years and is used for carbon dating but is not important for our purposes and makes up only a tiny proportion of all carbon.

During photosynthesis, the different masses of the carbon isotopes mean they do not react at the same rate, a consequence of the ¹³C–O bond in CO₂ being slightly stronger than a ¹²C–O bond. This causes all plant matter, and everything that consumes plant material, to be depleted in the heavier ¹³C isotope, although only by a very small amount, <0.1%. This ¹³C depletion is measurable in organic compounds by gas chromatography–combustion–isotope ratio mass spectrometry (GC-C-IRMS). Compounds are separated by GC, combusted completely to CO₂, and ionised and accelerated through a sector magnetic field

that resolves the different masses (strictly the mass to charge ratio, m/z) of CO₂ (with different combinations of oxygen and carbon isotopes) into three focused ion beams that are monitored by Faraday cups at masses 44, 45 and 46. By monitoring these three masses, the carbon isotopic composition of the CO₂, and hence the compound, can be fully determined. Partly owing to simplification of the measuring process and partly for historical reasons, carbon (and many other) isotope ratios are expressed in ‰ (per mille), relative to a standard, using the delta notation:

$$\delta^{13}\text{C} = \left(\frac{[^{13}\text{C}/^{12}\text{C}]_{\text{sample}} - [^{13}\text{C}/^{12}\text{C}]_{\text{standard}}}{[^{13}\text{C}/^{12}\text{C}]_{\text{standard}}} \right) \times 1000$$

The standard against which carbon isotopes are reported is a long-since-dissolved fossil cephalopod made of CaCO₃ called the Pee Dee Belemnite (PDB), which is the defined zero point.

The isotope discrimination during photosynthesis between the CO₂ in the air and plant organic matter (such as alkenone molecules) can be described by an ϵ (epsilon) factor, which in the case of photosynthesis is termed ϵ_p :

$$\epsilon_p = \left(\frac{[^{13}\text{C}/^{12}\text{C}]_{\text{carbon pool}}}{[^{13}\text{C}/^{12}\text{C}]_{\text{organic matter}}} - 1 \right) \times 1000$$

The ϵ term has the advantage of being in per mille, and the reconstruction of ϵ_p is the cornerstone of the alkenone CO₂ proxy.

converting the considerable energy delivered from the Sun into the chemical energy that fuels most life. The key enzyme in this reaction is called rubisco (ribulose-1,5-bisphosphate carboxylase oxygenase) and it is probably the most abundant and important enzyme on Earth. During the rubisco-mediated conversion of CO₂ into carbohydrate, ¹³CO₂ reacts more slowly than ¹²CO₂. This causes plant matter and, in fact, almost all organic matter on Earth to be somewhat depleted in ¹³C, as described in Box 1. It is the impact of this ¹³C-depleted signature of organic matter, released to the atmosphere during burning of fossil fuels, that confirms a human cause of increased *p*CO₂ over the past two centuries (Keeling *et al.*, 2010).

However, this isotope effect is not always the same. Over 30 years ago, algal ecologists and then geologists recognised that the full expression of the discrimination is an issue of supply versus demand. If organisms have either a large supply of CO₂ or a low demand for it, a large isotope discrimination is observed and vice versa (Laws *et al.*, 1995). Thus, if this relationship can be calibrated and the magnitude of the isotope effect can be measured in ancient rocks, we can estimate past *p*CO₂. The key to this determination is the use of chemical proxies that can be recovered from ancient sediments, attributed strictly to photosynthetic organisms, and for which δ¹³C values can be determined.

Calibrating the relationship

Growing cultures of algae indicates that there is a clear relationship between the carbon isotope effect that occurs during photosynthesis (ϵ_p) and CO₂ concentrations:

$$\epsilon_p = \epsilon_f - \frac{b'\mu}{[\text{CO}_2(\text{aq})]} \quad (1)$$

where ϵ_f is the maximum discrimination of the rubisco enzyme in an organism, μ is the growth rate of the organism and b' is a species-dependent coefficient that reflects the various physiological factors that govern how CO₂ is transported from the environment into the cell and to the site of carbon fixation (adapted from Bidigare *et al.*, 1997). Equation 1 reflects the combined effect of supply versus demand, represented by the concentration of CO₂ and the algal growth rate, respectively (Figure 1). Note the fact that, at high supply versus demand, the isotope effect tends

towards ϵ_f and that, at low supply versus demand, it tends towards zero.

However, the relationship differs between organisms. In particular, not all organisms rely on diffusion of CO₂ across the cell membrane; some actively concentrate CO₂ (Laws, Bidigare and Popp, 1997). There are still complications that arise for those organisms that rely on diffusion across the cell membrane. A cell with a large surface area (*SA*) relative to its volume (*V*) effectively has a higher supply to demand ratio, and in fact that component can be extracted from the b' term in Equation 1 to yield

$$\epsilon_p = \epsilon_f - \frac{b''\mu}{[\text{CO}_2(\text{aq})]} \frac{V}{SA} \quad (2)$$

Thus, we need to calibrate the above relationship for a specific organism. Most work has been conducted on an organism known as *Emiliania huxleyi*, a type of algae that is common in today's oceans and forms magnificent shells made of CaCO₃ plates called coccoliths (see, for example, Bidigare *et al.*, 1997). These organisms are widespread in the oceans (Figure 2), and either *E. huxleyi* or their close relatives have existed for tens of millions of years.

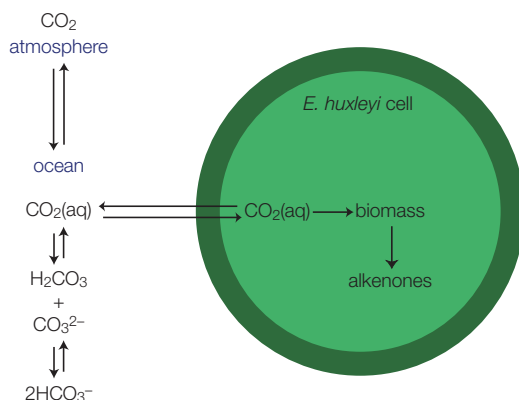


Figure 1 A cartoon of a cell showing the key processes that dictate carbon isotope discrimination during photosynthesis: diffusion of CO₂ into the cell and CO₂ fixation by rubisco. The rates of the two reactions are largely governed by CO₂ concentration and the algal growth rate, respectively. If the former is slow such that the rate of diffusion is low compared with the rate of fixation, the cell essentially becomes a closed system; that is, *all* of the CO₂ that diffuses into the cell is assimilated and there is no isotope discrimination.



Figure 2 A bloom of coccolithophores, predominantly *Emiliania huxleyi*. Although individually tiny, the dramatic effect of coccolithophores on the carbon cycle can be seen in this false-colour Landsat 7 image. Taken on 24 July 1999, it shows a massive bloom of coccolithophores off the coast of southwest England. The milky blue material is actually the remains of dead individuals, a vast number of calcite coccolith plates, each only a few microns across. Image courtesy of the NERC Earth Observation Data Acquisition and Analysis Service, Plymouth.

Measuring past $p\text{CO}_2$

The most crucial aspect of exploiting the relationship between $p\text{CO}_2$ and carbon isotope discrimination by *E. huxleyi* in ancient sediments is being able to measure the carbon isotopic composition of organic matter that can be unambiguously assigned to these organisms. This is actually much trickier than it sounds. Ancient sediments or rocks can contain a significant amount of organic matter dispersed among the mineral grains; in fact, it is the thermal maturation of this organic matter that results in the formation of fossil fuel deposits. However, that organic matter derives from a great variety of plankton as well as other inputs including land plants and animal or bacterial sources.

The carbon isotopic composition of haptophyte biomass

Fortunately, *E. huxleyi* and its close relatives synthesise a rather unusual group of compounds called alkenones – long-chain polyunsaturated hydrocarbons with a ketone group (Figure 3).

These compounds are very uncommon in nature and their presence, concentrations and isotopic compositions in sediments can be diagnostically assigned to *E. huxleyi* or closely related organisms. Compounds in sedimentary materials used in this way are generally termed biomarkers.

The challenge, therefore, is in being able to measure the carbon isotopic composition of these biomarkers in ancient sediments of known age and whose geology of formation are known. To do this, the compounds are first extracted from ground sediments using organic solvents in a process somewhat analogous to brewing tea. The complex diversity of extracted compounds is then simplified by removing highly complex macromolecules and by splitting these into different fractions according to their polarity (for example, alkanes, ketones and alcohol fractions). These fractions can then be analysed using a gas chromatograph (GC) interfaced to an isotope ratio mass spectrometer (IRMS). The GC comprises an oven containing a long (c. 30 m) capillary column bearing a stationary phase with which organic

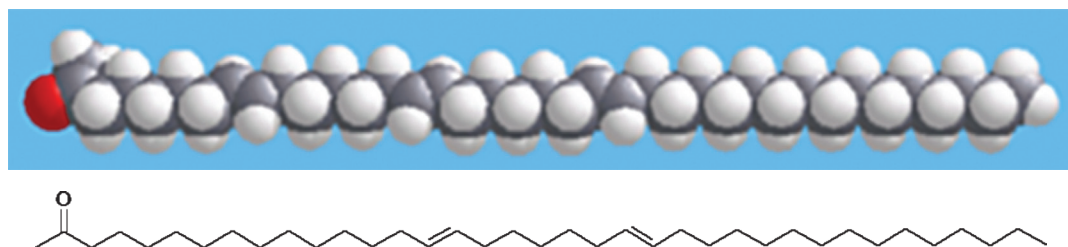


Figure 3 The alkenone, a long-chain partially unsaturated ketone present only in some species of haptophyte algae. Alkenones were identified by researchers at the University of Bristol in the early 1980s (Volkman *et al.*, 1980).

compounds interact; helium flows through the column and, as the oven temperature increases, progressively higher molecular weight compounds become volatile and are carried by the helium stream through the system to the IRMS. The mass spectrometer measures the ratio of ¹³CO₂ to ¹²CO₂, and so the compounds eluting from the GC must be oxidised (combusted) between the GC and IRMS (Hayes *et al.*, 1990), hence GC-C-IRMS. Thus, sediments containing the ancient molecular fossils of *E. huxleyi* can be extracted, the alkenones partially isolated in a ketone fraction, and their carbon isotopic composition determined by this technique.

Calculating ϵ_p values

ϵ_p represents the difference between the isotopic composition of *E. huxleyi* and the CO₂ from which it grew. The former is determined by using the $\delta^{13}\text{C}$ values of alkenones and assuming that they can be used to represent (after minor correction) the source organism's overall carbon isotopic composition. The latter is achieved by measuring the $\delta^{13}\text{C}$ value of the CaCO₃ fossil shells of planktonic marine organisms; typically, fossils of planktonic heterotrophs called foraminifera are employed owing to their widespread occurrence, abundance and well-studied ecology. Some additional temperature- and salinity-based corrections are required because isotope discrimination also occurs between CO₂ and CO₃²⁻ and between CO₃²⁻ and the CaCO₃ during mineral formation.

Converting ϵ_p records into $p\text{CO}_2$ records

The final aspects of generating a $p\text{CO}_2$ record are related to understanding the geological context of the study site. Equation 2 shows that the relationship between ϵ_p values and CO₂ concentration is dependent on algal growth rates. Therefore, we must select our target sediments carefully and

understand the likely ecology of the organisms living in the overlying water: were they associated with high nutrient concentrations and thus high growth rates or were nutrient concentrations low and the organisms growing slowly? There is a variety of tools that can be used to explore this, for example the number of fossils or amount of organic matter in the sediments, but this can be a challenge.

After all of this work, we can finally solve Equation 1 for the concentration of CO₂ in seawater at that particular site ([CO₂(aq)]). This is not the same as the partial pressure of CO₂ in the atmosphere ($p\text{CO}_2$), which is our actual target. The conversion from [CO₂(aq)] to $p\text{CO}_2$ is rather straightforward and governed by Henry's law: for a given temperature, the amount of a gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid:

$$p = k_{\text{H}}c \quad (3)$$

where k_{H} is the temperature-dependent equilibrium constant for any gas partitioned between a gas and a liquid and substituting p for $p\text{CO}_2$ and c for [CO₂(aq)]. Therefore, determining $p\text{CO}_2$ requires an independent proxy for past ocean temperatures, a topic of considerable interest in its own right. An additional assumption here is that the ocean is in equilibrium with the atmosphere, which is not always the case and again requires an understanding of the geological setting.

In summary (Figure 4), alkenone $\delta^{13}\text{C}$ values are used to determine $\delta^{13}\text{C}$ values of haptophytes and foraminiferal $\delta^{13}\text{C}$ values are used to determine $\delta^{13}\text{C}$ values of dissolved CO₂. The two together are used to calculate ϵ_p values, which is then related to [CO₂(aq)] via Equation 1 and well-studied relationships for *E. huxleyi* determined in cultures and in modern oceans, but only if growth rate is

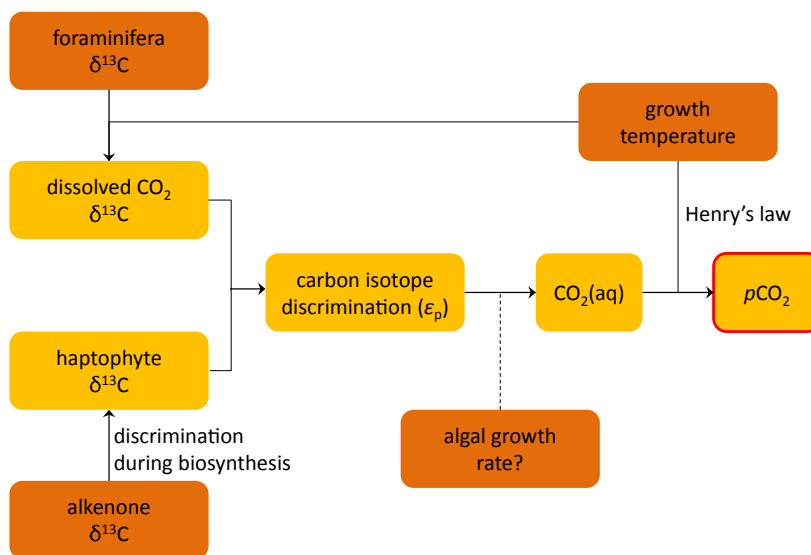


Figure 4 A guide to reconstructing ancient $p\text{CO}_2$ levels from the determination of alkenone and foraminiferal $\delta^{13}\text{C}$ values. Quantities in orange boxes are things that must be measured or inferred and those in yellow are calculated.

constrained. Finally, $p\text{CO}_2$ can be calculated, using temperature estimates and assuming equilibrium between the atmosphere and ocean. This is a challenging effort that requires a great deal of investigation but is rewarding owing to the range of techniques employed and the necessary integration of biological, chemical and geological disciplines.

What do the combined ice core and alkenone isotope record reveal?

The last 800 000 years

By using instrumental, ice core and alkenone isotope records, we now have a record of the broad changes in atmospheric CO_2 over the past 45 million years. Instrumental records have shown that over the last century atmospheric $p\text{CO}_2$ has risen substantially as anthropogenic CO_2 has been released by the burning of fossil fuels. The ice core records show that present-day $p\text{CO}_2$ is far higher than at any point during our current climatic 'mode' of glacial–interglacial cycles (Petit *et al.*, 1999; Siegenthaler *et al.*, 2005; Luthi *et al.*, 2008).

The ice core records also show that for the past 800 000 years atmospheric $p\text{CO}_2$ has swung repeatedly between a maximum of 300 ppm during interglacial periods to a minimum of 180 ppm during the peak of ice ages (Petit *et al.*, 1999; Siegenthaler *et al.*, 2005). The swings are

paced by the regular beat of variations in the shape of the Earth's orbit around the Sun, and the glacial–interglacial cycles follow a stable 100 000 year periodicity. However, these $p\text{CO}_2$ swings do not appear to be the ultimate driver of the shifts between glacial and interglacial periods: $p\text{CO}_2$ either closely follows or slightly lags behind changes in ice volume and temperature. If $p\text{CO}_2$ were the ultimate driver of the ice volume changes then it would be expected to lead rather than follow changes in ice sheets. The absence of a time lag between $p\text{CO}_2$ and ice volume suggests that the ice volume change is driving the $p\text{CO}_2$ shift. But this does not mean that $p\text{CO}_2$ changes did not influence climate; instead, it appears that they acted as a positive feedback. As ice sheets began to retreat, $p\text{CO}_2$ decreased, and the associated cooling effect caused an initially small decrease in ice sheet size to be amplified.

The Pliocene – the most recent warm geological epoch

The Pliocene is a geological epoch that spans a period of time from 5.3 to 2.6 million years ago. It was a time of little ice in the Arctic Ocean or on Greenland, fewer mountain glaciers and warmer temperatures globally compared with today. The large 100 000 year oscillations in ice volume, which characterised the last million years, did

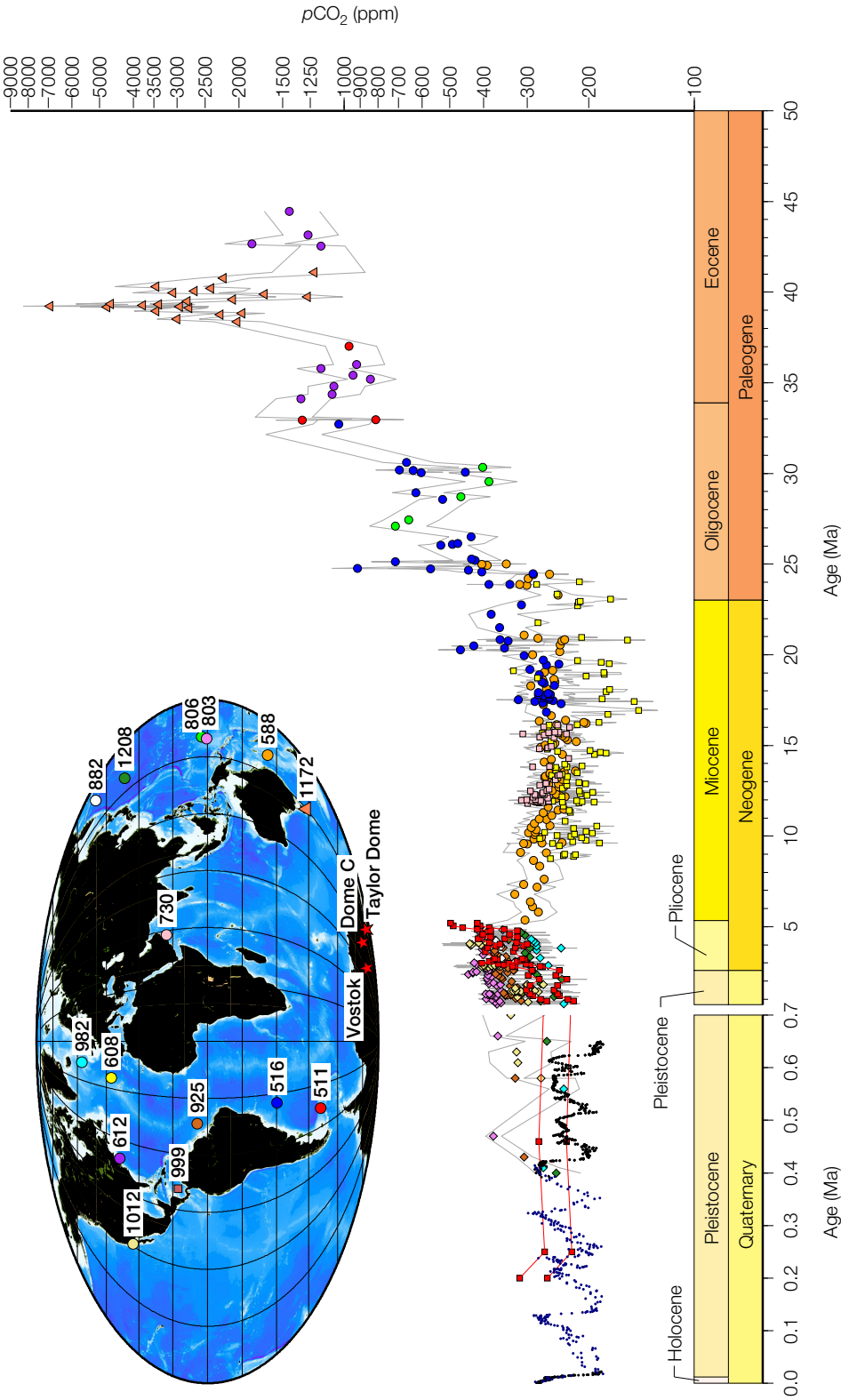


Figure 5 A reconstruction of $p\text{CO}_2$ based on ice core (last 650 000 years) and sedimentary alkenone $\delta^{13}\text{C}$ values (45 million years). The timescale is amplified to highlight the 100 000 year glacial and interglacial cycles for the past ~1 million years but also shows the long-term decrease in $p\text{CO}_2$ during the Cenozoic. Data from Bijl *et al.*, 2009; Hendericks and Pagani, 2008; Monnin *et al.*, 2004; Pagani, Arthur and Freeman, 1999; Pagani *et al.*, 2005; Pagani *et al.*, 2009; Petit *et al.*, 1999; Seki *et al.*, 2010 and Siegenthaler *et al.*, 2005.

not occur. Because ice core $p\text{CO}_2$ records do not extend far enough back in time to capture the Pliocene, the alkenone-based approach has been used instead (Pagani *et al.*, 2010; Seki *et al.*, 2010).

Alkenone-based $p\text{CO}_2$ estimates confirm that the warm Pliocene was accompanied by $p\text{CO}_2$ levels slightly higher (300–400 ppm; Figure 5) than recorded during the glacial–interglacial cycles of the last million years, and probably similar to the levels in the atmosphere today. These reconstructions also show that there was a gradual drop in $p\text{CO}_2$ and temperature from the Pliocene to the present day. This coeval drop in temperature and $p\text{CO}_2$ allows estimation of ‘climate sensitivity’ – the level of warming which occurs in response to a doubling of $p\text{CO}_2$. Due to feedbacks within the Earth's climate system (such as those occurring on glacial–interglacial timescales mentioned above), climate sensitivity represents a broader range of climate forcings than would be expected from the $p\text{CO}_2$ greenhouse effect alone. We therefore can use the geological record to constrain this term, which is an important parameter in many computational climate models used to predict future climate change. Crucially, alkenone data for the Pliocene suggests that climate sensitivity at this time was much larger than in modern times with significant ~3 °C warming resulting from only slightly elevated $p\text{CO}_2$ levels relative to modern times.

The Cenozoic – from greenhouse to icehouse

The Cretaceous, the geological epoch that ended more than 65 million years ago, was largely a ‘greenhouse’ climate with little or no ice at either pole and temperatures significantly higher than today. At this time, most of Great Britain was under water, bathed by a warm shallow sea in which the massive chalk deposits that underlay much of the southeast of England were formed. The change from the warm ‘greenhouse’ of the Cretaceous to the ‘icehouse’ climate of the present day took much of the 65 million years that followed the Cretaceous, and particularly the past 50 million years. Climate reconstructions based on the oxygen isotope composition of microfossils show that the descent into the icehouse during the Cenozoic (the name for the era comprising the last 65 million years) happened in a number of ‘steps’, with dramatic changes in climate happening over (geologically) short periods of time. Alkenone-based $p\text{CO}_2$ reconstructions now span the past 45 million years, allowing the relationship

between changes in the global climate state and $p\text{CO}_2$ to be examined.

The alkenone-based $p\text{CO}_2$ record (Figure 5) shows a decline broadly similar to the oxygen isotope temperature records in marine carbonates. $p\text{CO}_2$ declined rapidly during the Oligocene (34–23 million years ago) from well over 1000 ppm during the warmth of the Eocene (56–34 million years ago) to less than 500 ppm. This was followed by a further gradual decrease until the start of the Miocene (23 million years ago), when $p\text{CO}_2$ reached ~300 ppm – slightly higher than today. Such changes suggest that a long-term decline in $p\text{CO}_2$ is the primary climate driver that caused the descent into the icehouse. However, since the Miocene, the record shows that $p\text{CO}_2$ levels have been relatively stable, despite significant changes in climate since the Miocene, including the growth of the East Antarctic Ice Sheet (at ~14 million years ago) and the growth and intensification of northern hemisphere glaciation in the Pliocene. The apparent stability of $p\text{CO}_2$ for the last 14 million years has caused some problems for climate scientists, who assumed that most of the major events during the descent into the icehouse would be accompanied by major $p\text{CO}_2$ decreases. However, it appears that the climate system may have various $p\text{CO}_2$ ‘thresholds’ that allow for climatic deterioration to happen but don't necessarily trigger it. Instead, $p\text{CO}_2$ sets the stage (conditions the Earth system), causing the system to be poised for other factors, such as ocean gateway closings or astronomical forcing, to trigger sudden and dramatic change. More recently, close investigation of some of these events (Pearson, Foster and Wade, 2009) has also shown that there may be subtle changes in $p\text{CO}_2$ that were missed in the early, relatively low temporal resolution studies, further suggesting a climate system defined by multiple thresholds or tipping points.

Conclusion

The alkenone palaeobarometer has allowed a record of atmospheric CO₂ to be generated for the past 45 million years. Although the approach requires the measurement of multiple variables, each associated with both analytical uncertainty and significant assumptions, it has allowed the $p\text{CO}_2$ record to be extended far beyond the ~1 million year time span for which we have ice

cores. The records show the expected decline in $p\text{CO}_2$ as the Earth's climate deteriorated from the warmth of the Cretaceous to the icehouse of today, but the detail of the record and the apparent stability of the past 20 million years continue to challenge our understanding of the reaction of the Earth's climate to greenhouse gas forcings. The alkenone palaeobarometer is the result of the synergy of work from disparate scientific communities including biologists,

physical and chemical oceanographers, and Earth scientists. The records produced have demonstrated the sensitivity of the Earth's climate system to changing concentrations of $p\text{CO}_2$ over the geological past and highlighted its likely importance in the future. Ongoing research refining the proxy and generating new and more accurate records will continue to inform modellers of future climate of the sensitivity of the Earth system to greenhouse gas.

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Marcus Badger was a researcher at the Bristol Biogeochemistry Research Centre, School of Chemistry, at the time of writing and is now is a lecturer at the Department of Earth Sciences, University of Bristol. Email: marcus.badger@bristol.ac.uk

Richard Pancost is a professor of biogeochemistry at the Bristol Biogeochemistry Research Centre, School of Chemistry, University of Bristol. Email: r.d.pancost@bristol.ac.uk

Tim Harrison is the School Teacher Fellow and Director of Outreach, School of Chemistry, University of Bristol. Email: t.g.harrison@bristol.ac.uk